

STRUCTURAL CHANGES ON HEATING AND HIGH-TEMPERATURE DEFORMATION OF COMPOSITES BASED ON PYROPHYLLITE RAW MATERIAL FROM THE KUL'-YURT-TAU DEPOSIT

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The changes occurring when composites based on pyrophyllite raw material, obtained from the Kul'-Yurt-Tau deposit, with phosphate binder are heated are studied. Their compaction and hardening are strongly affected by processes associated with the interaction of the ancillary rocks with the phosphate binder. The deformations of composites in two temperature regimes are studied: heating with the temperature changing at a constant rate and with isothermal soaking. The experimental results make it possible to predict the behavior of the materials during operation in the thermal units of different systems and optimize materials preparation in the process of manufacturing articles with prescribed characteristics.

Key words: composite, pyrophyllite, phosphate binder, structure, deformation, heating.

Pyrophyllite raw material from the Kul'-Yurt-Tau deposit can be used to prepare composites based on phosphate binders [1, 2]. It is as good as the pyrophyllite from the Ovruchskoe deposit, which in the past was usually used in ceramic production.

The purpose of the present work is to study the behavior of composites based on pyrophyllite material and phosphate binder on heating.

Ordinarily, hydration-hardening compositions based on phosphate binders are used in the form of mixtures and molded articles. In the latter case they acquire construction strength either directly during hardening or on heating to comparatively low temperatures (300 – 600°C). Just as in [2], the behavior of mixtures with phosphate binder based on quartz-pyrophyllitic schists and pyrophyllitic rocks, whose chemical and mineral compositions are presented in [1], were studied.

Structure. Hardening of the composites studied is due to complex physical-chemical transformations of their components [3]. At temperatures to about 900°C water is gradually

removed from materials, and chemical interactions occur between the filler and binder in the process. To 450°C water removal is due to polycondensation of phosphates introduced by the binder and formed in rock as a result of the interaction of the binder with the minerals. The binder interacts with diaspore and other minerals above all, while the pyrophyllitic phase is most stable. Above 450°C water is released from the remainder of the pyrophyllite-diaspore rocks that has not reacted with the binder.

At temperatures to 700°C embryos pass through a polymerization stage (polycondensation), which is followed by disordering at temperatures 700 to 1200°C, since the polymer structure breaks down and, in addition, polymorphic transformations of phosphates occur. At the same time, above 1000°C, when a liquid phase appears, sintering occurs, which results in compaction and hardening of the structure. Evaporation of low-melting impurities, volatilization of phosphorus pentoxide and destruction of polyphosphates occur above 1300°C.

The products of the interaction of the components are x-ray amorphous to temperature 300°C, above which lines due to aluminum metaphosphate $\text{Al}(\text{PO}_3)_3$ and AlPO_4 appear in the x-ray diffraction patterns. Lines due to AlPO_4 , cristobalite and silicon pyrophosphate SiP_2O_7 are found above 1200°C.

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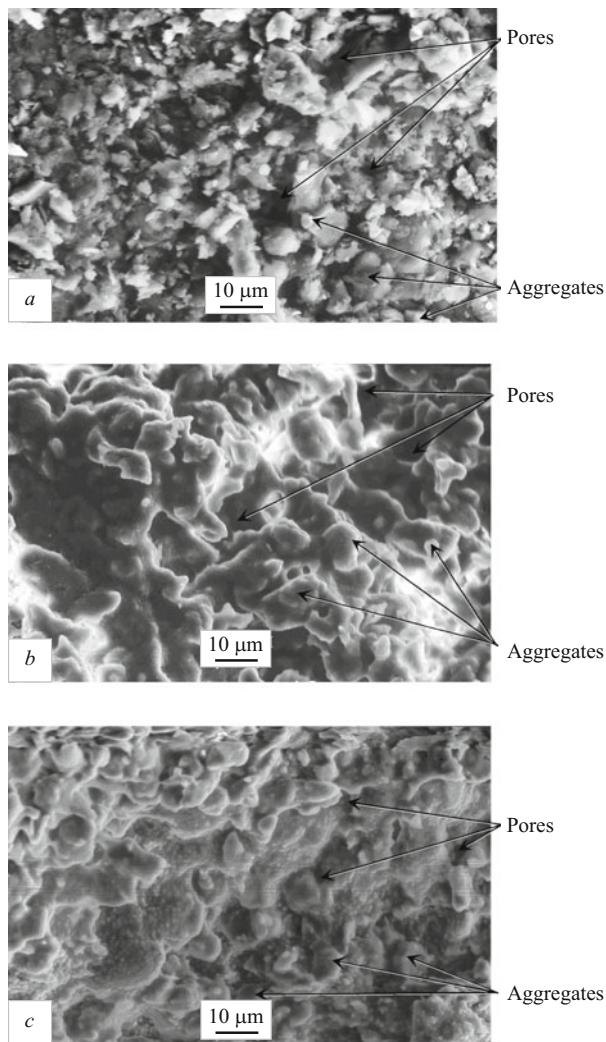


Fig. 1. Microstructure of composites after treatment at temperatures: a) 300°C; b) 1000°C; c) 1400°C. $\times 550$.

In summary, the hardening of the compositions studied is based on the formation of different polyphosphates as a result of the chemical interaction of H_3PO_4 with the components of pyrophyllitic material.

The microstructure of the samples was studied with a scanning electron microscope. The composites have a porous uniform structure at all treatment temperatures (Fig. 1). Above 300°C embryos combine into large aggregates and have no sharp interfaces, which is an indication of the presence of an amorphous phosphate binder in them. Treatment at 1000 and 1400°C results in larger aggregates, sharp interfaces with pores appear, and at 1000°C the sample differs by the presence of larger channel pores. Ultimately, as a result of the formation of a direct (ceramic) bond a strong structure forms because of the interaction between the phosphate binder and a finely disperse filler; this structure determines the technical characteristics of the composite.

Up to treatment temperature about 900°C uniformly distributed filler particles and pores are clearly seen in the struc-

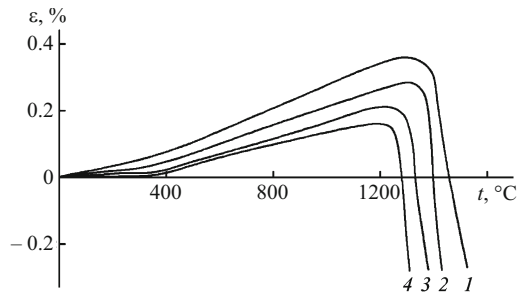


Fig. 2. Deformation of composites under loading: 1) no load; 2) 0.2; 3) 0.4; 4) 0.6 MPa.

ture of the composition with unfired, finely ground powder; subsequently, boundaries are observed between them. When fired raw material is used as a finely ground component the structure of the composite above 1200°C is characterized by the presence of denser aggregates of the binder adjoining the filler; the samples have fewer pores, which are distinguished by their small size.

In a composition with higher granular filler content (to 70%), because the filler has a reinforcing effect the material becomes stronger, and the shrinkage due to heat treatment and the porosity decrease. The composite material obtained has a uniform structure. In the grain-binder contact zone sintering occurs under the action of temperature because the components of the binder interact with one another and because of adhesion and cohesion processes.

Thus, aluminum and silicon phosphates form when pyrophyllitic material interacts with the phosphate binders. Above 1100°C these phosphates and a glass phase strengthen the components of the composite, which determine the strength properties of the materials.

A scheme for producing refractory articles, taking account of the particulars of the thermal transformations in composites, has been proposed. A manufacturing line for such articles has been designed.

Deformation. As a rule, the processes studied are accompanied by a change of volume, which can be measured dilatometrically.

First, the deformation occurring under heating and loading (GOST 4070–2000) was determined in order to find the temperature range for subsequent creep tests and determine the required load level and rate of temperature increase to isothermal regimes. The choice of temperature range (1250–1450°C) for studying creep in accordance with GOST 25040–81 is based on the fact that the deformation under a load over 12 h does not exceed 1% in this range.

To impart initial strength all samples were pre-heat-treated at 300°C and when necessary to the working temperatures. Preliminary heating was done mainly without a load. The testing method and apparatus are presented in [4].

The typical deformation curves for samples, based on fine-grain pyrophyllite, under different loads are shown in Fig. 2. A change of the rate of ordinarily thermal expansion

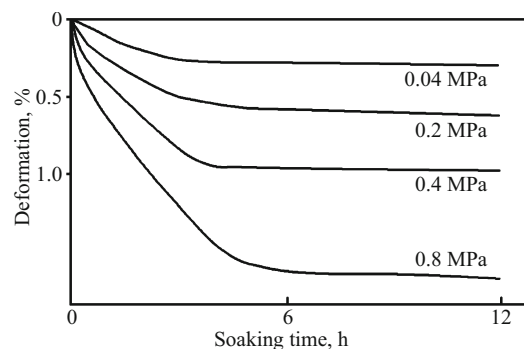


Fig. 3. Creep deformation of composites under different loads and test temperature 1250°C.

in the temperature range 400 – 500°C due to water release was observed on all curves. The structural changes due to polycondensation, formation of polyphosphates and other transformations are not manifested in the deformation curves. We note that the expansion of a sample depends on the load: the greater the load, the smaller it is. The compression onset temperature of composites affects their pre-heat-treatment temperature: a stable structure forms above about 850°C (1 h soaking).

Generalizing the creep data obtained for fine-grain samples, their behavior at temperatures to 1450°C and loads to 0.8 MPa can be characterized as follows. The deformation increases by a factor of 1.5 – 2 (at 1350°C) with the load increasing from 0.2 to 0.4 MPa and very little from 0.4 to 0.8 MPa. With isothermal soaking for 12 h a steady creep regime starts (at 1350°C) irrespective of the load. The deformation of all compositions is least at 1250°C for all loads and increases by a factor of approximately 2.5 with temperature increasing to 1450°C. An example of creep curves is presented in Fig. 3.

The deformation on heating and the creep of composites with coarse-grain filler differ from the behavior of the compositions studied. Because pyrophyllite is present the experimental composites are not as highly refractory as, for example, corundum, since their softening temperature decreases to 1320°C. This is due to the presence of impurities in the initial raw material, which results in the formation of a significant amount of liquid phase with low viscosity and, correspondingly, causes the sample to expand soon after it starts to deform. The introduction of the corundum filler increases the deformation onset temperature to 1450 – 1550°C.

Creep deformation of corundum-pyrophyllitic compositions occurs at lower temperatures (1350 – 1450°C) than corundum compositions; in the presence of a liquid phase creep appears by means of slipping of grains in an amorphous matrix. The tests showed that creep is greater than in corundum compositions based on phosphate binders [3]. This is explained by the appearance of a liquid phase in corundum-pyrophyllite composition as a result of the formation in it of

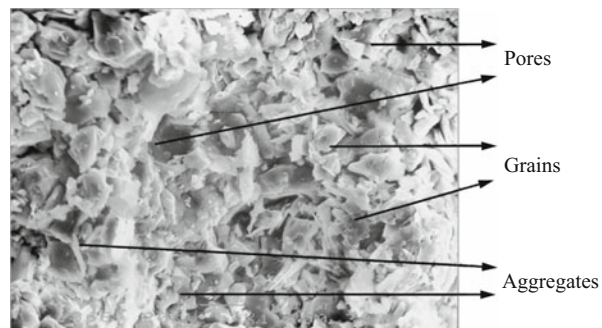


Fig. 4. Microstructure of compositions pyrophyllite–orthophosphoric acid after creep tests; ×1100.

silicon phosphate $\text{Si}_3(\text{PO}_4)_4$, whose melting temperature is 1150°C.

Compositions based on quartz-pyrophyllite material show lower deformation onset temperatures on heating (1380 – 1430°C), which is due to the formation of low-melting silicon-phosphates and a glassy phase.

After creep tests at 1350°C (Fig. 4) the composite possesses cellular structure with slit-shaped pores. The deformation process during creep is accompanied by shrinkage of the sample, and the open porosity and average pore size decrease. Thus, the evolution of the structure of the material under load (in the presence of a liquid phase) results in characteristic changes in the fragments.

During high-temperature creep structural transformations occur mainly by volume redistribution of the binding phase — low-melting component. The sample deforms owing to a change in the size of grains and their aggregates as well as to deformation of the phosphate binder. The magnitude of the deformation depends on the temperature and load. For example, under load 0.14 MPa it is 0.5% at 1200°C, 0.8% at 1300°C and 0.9% at 1450°C.

To secure the required operating properties composites can be determined into three groups by their formation temperature: 1) treatment at room temperature; 2) low-temperature treatment at temperatures to 200 – 600°C (less often to 300°C); 3) high-temperature treatment at temperatures to 1000 – 1300°C.

The same deformation behavior is characteristic for the materials in the first group, since on heating to the temperatures of creep tests approximately the same physical-chemical processes occur in them (above 300°C). High-temperature treatment imparts a more stable structure to composites in the third group, and processes that stabilize the phase composition can occur in them. Specifically, when an equilibrium structural state of a composite material is reached the character of the creep regularities approaches that of kilned materials.

The test results presented above make it possible to identify three temperature intervals of deformation with very different behavior of the samples: 1) low-temperature — to

1100°C; 2) medium-temperature — from 1100 to 1300°C; 3) high-temperature — above 1300°C.

During heating and creep tests the phase content of a composition changes continually: water removal, polymerization of silicon phosphates in the interval 400 – 700°C and then decomposition of silicon phosphates with phosphorus pentoxide released. The latter compound interacting with silica filler forms additional silicon phosphate up to 1120°C. Phase transformations and chemical interactions of the components with low-melting or amorphous phases being formed make it possible for filler grains to slip in an unstable creep period. The conditions for this mechanism to occur in a stable period are lower cohesion strength of the interparticle (phosphate) binding phase compared with the filler and phosphates being able to participate in plastic flow. After heat treatment at 600°C the cohesion forces of the binding phase are weaker than its adhesion binding with the filler grains; after 900°C the adhesion forces between the binder and filler and cohesion of the binder are close to one another. Therefore, at temperatures to 1100°C in composite materials based on phosphate binders grain slip can occur by means of displacements of a grain relative to the binding phase and together with the surface layers of the binder.

In the medium-temperature interval creep in an unstable period increases (during 12 – 16 h) under the action of even low stresses (0.1 – 0.2 MPa). The main deformation mechanism is slip of filler grains. This mechanism is activated by an increase of the formation rate of silicon-phosphate glass. These processes are extended in time, and their duration as a function of the test temperature can change from 100 h at temperatures up to 1100°C to several hours (above 1300°C).

Phase transformations are not observed in the high-temperature interval (1350 – 1550°C). All components of a composition are in crystalline and amorphous states. Creep occurs under the action of three processes: diffusion-viscous flow, filler-grain slip and sintering. The predominance of any process is determined by the magnitude of the applied load and temperature.

The results obtained agree with previously established regularities and particularities of the creep of oxide, nitride and oxide-nitride compositions, i.e., creep depends little on the chemical nature of the filler. The hardening mechanism in these materials is the same and it depends substantially on the chemical-mineralogical composition and dispersity of the fillers, the presence of impurities in the initial components, the degree of chemical interaction between the filler and phosphate binder and the treatment temperature. The experi-

mental results make it possible to optimize the conditions for fabricating materials with prescribed properties and to predict the behavior of materials during service in thermal units, specifically, their service life at high temperatures under a mechanical load.

CONCLUSIONS

Structure forming processes in compositions based on pyrophyllitic materials on heating were studied. It was determined that hardening in these systems is a result of the interaction of pyrophyllite with phosphate binder at temperatures above 300°C. The phase composition of the composites was studied. On heating sintering due to the binder components as well as adhesion processes is observed in the grain-binder contact zone. A transformation of the aluminum and silicon phosphates of different modifications and melting of silicon pyrophosphate occur in the binder; thermal transformations in the filler intensify sintering.

The deformation of the composites as a function of the test temperature proceeds by three mechanisms: slip of filler grains (this occurs at all three test temperatures); diffusion-viscous flow, which plays a substantial role above 1000°C; and, sintering, which starts at 1100°C. When a liquid phase arises viscous flow can appear. A sharp increase of creep in the interval 1150 – 1200°C is characteristic for compositions; when 30 – 60% coarse-grain filler is introduced, the deformation stability of the material increases.

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